

THE SYNTHESIS OF DERIVATIVES OF
CHRYSENE

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WILLIAM SCOTT STRUVE

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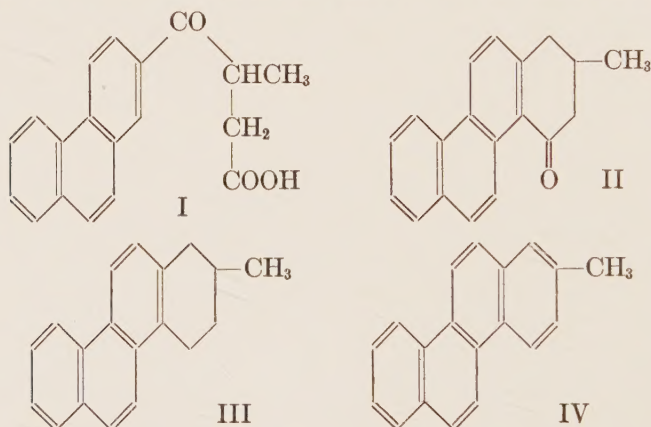
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THE SYNTHESIS OF DERIVATIVES OF CHRYSENE

W. E. BACHMANN AND W. S. STRUVE*

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Three years ago¹ we described the preparation of β -(2-phenanthroyl)-butyric acid (I), which we prepared from 2-propionylphenanthrene as an intermediate in the synthesis of 2-methylchrysene (IV)[†]. We have now completed the projected synthesis, using the well-known steps of the



Haworth method.² Clemmensen reduction of the acid yielded γ -(2-phenanthryl)- β -methylbutyric acid, which was cyclized in the form of its acid chloride by means of stannic chloride. Under the conditions employed cyclization took place nearly entirely from the 2 to the 1 position with the formation of 2-methyl-4-keto-1,2,3,4-tetrahydrochrysene (II), although there appeared to be present some of the cyclic ketone formed by cyclization to the 3 position. 2-Methyltetrahydrochrysene (III) was obtained from the cyclic ketone by Clemmensen reduction, and the resulting hydrocarbon was dehydrogenated smoothly to 2-methylchrysene by palladium on charcoal. The 2- and 3-propionylphenanthrenes, which we

* From the Ph.D. dissertation of W. S. Struve.

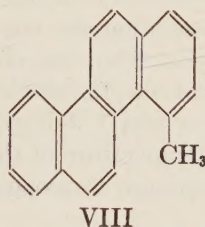
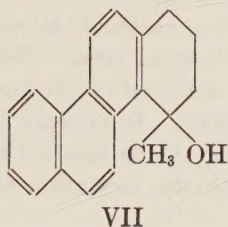
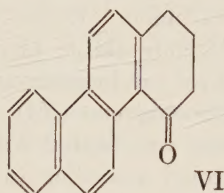
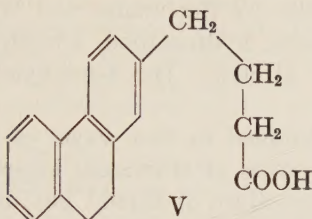
[†] The numbering system for the chrysene molecule is that used in the index of *Chemical Abstracts*.

¹ BACHMANN AND STRUVE, *J. Am. Chem. Soc.*, **58**, 1659 (1936).

² HAWORTH, *J. Chem. Soc.*, **1932**, 1125.

had prepared from phenanthrene and propionyl chloride, have now been reduced by the Clemmensen method to the corresponding 2-*n*-propylphenanthrene and 3-*n*-propylphenanthrene.

We have also prepared 4-methylchrysene (VIII) from the cyclic ketone, 4-keto-1,2,3,4-tetrahydrochrysene (VI). The latter compound was made by Haworth³ from 2-acetylphenanthrene. We have made use of the γ -[2-(9,10-dihydrophenanthryl)]-butyric acid (V) of Burger and Mosettig,^{4,5} which is readily obtained by Clemmensen reduction of the corresponding keto acid, which in turn can be prepared in excellent yields by interaction of 9,10-dihydrophenanthrene and succinic anhydride. The dihydrophenan-



thrylbutyric acid was dehydrogenated in the form of its methyl ester with palladium on charcoal at a relatively low temperature (240–260°) in excellent yields (90–95 per cent.). At this temperature the hydrogen was eliminated rapidly and the yield was much higher than was the case when the free acid or its methyl ester was dehydrogenated at a higher temperature (300–320°), the yield under these conditions being only 20–40 per cent.

The γ -(2-phenanthryl)butyric acid was cyclized by treating the acid chloride in benzene solution in the cold with stannic chloride. This procedure gives the 4-keto-1,2,3,4-tetrahydrochrysene in better yields than the Haworth³ method of cyclization with sulfuric acid and does not require repeated recrystallizations in order to obtain the cyclic ketone in a pure form. When the cyclization was carried out at room temperature, a

³ HAWORTH AND MAVIN, *ibid.*, **1933**, 1013.

⁴ BURGER AND MOSETTIG, *J. Am. Chem. Soc.*, **59**, 1302 (1937).

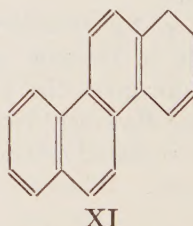
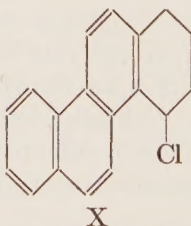
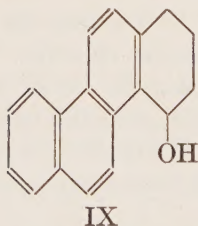
⁵ FIESER AND JOHNSON, *ibid.*, **61**, 168 (1939).

mixture of cyclic ketones was obtained which probably contained the isomeric compound formed by cyclization to the 3 position, although no attempt was made to isolate the product. Clemmensen reduction of the 4-ketotetrahydrochrysene yielded a crystalline tetrahydrochrysene, which could be dehydrogenated to chrysene by palladium on charcoal at a temperature of 300–320°.

4-Methyl-4-hydroxy-1,2,3,4-tetrahydrochrysene (VII) was prepared by interaction of the cyclic ketone with methylmagnesium iodide. The crystalline carbinol was simultaneously dehydrated and dehydrogenated to 4-methylchrysene in 92 per cent. yield by the action of palladium on charcoal, the method used successfully by Bachmann and Wilds⁶ on a number of carbinols. Unlike the parent hydrocarbon, 4-methylchrysene forms a relatively stable picrate in alcohol. The 4-methylchrysene is being tested for carcinogenic activity.

1,2-Dihydrochrysene (XI) was obtained in two ways. 4-Ketotetrahydrochrysene was heated with an excess of aluminum isopropoxide in *n*-propyl alcohol according to the procedure of Lund,⁷ but under these conditions no reduction took place. When the reaction was carried out in boiling toluene solution the corresponding carbinol, 4-hydroxy-1,2,3,4-tetrahydrochrysene (IX), was obtained in good yield. When xylene was substituted for toluene, the carbinol was obtained in two runs; in six other runs the product was 1,2-dihydrochrysene. It appears that prolonged heating at the temperature of the boiling xylene resulted in the splitting off of basic aluminum isopropoxide with the formation of the dihydrochrysene.

The 4-hydroxytetrahydrochrysene readily forms a methyl ether by the action of methanol containing a small amount of sulfuric acid and gives an acetate with acetic anhydride in pyridine. By treatment of a benzene solution of the carbinol with hydrogen chloride gas the carbinol yielded 4-chlorotetrahydrochrysene (X). 1,2-Dihydrochrysene can be obtained from the chloride by treatment with pyridine at the boiling point of the solution.



⁶ BACHMANN AND WILDS, *ibid.*, **60**, 624 (1938).

⁷ LUND, *Ber.*, **70**, 1520 (1937).

As was expected, the dihydrochrysene is readily dehydrogenated to chrysene.

Experiments are in progress on the condensation of the 4-chlorotetrahydrochrysene with sodio-malonic ester. With the acetic acid group in the 4 position it should be possible to prepare derivatives of 3,4-benzpyrene by cyclization of the acid and treatment of the cyclic ketone with various reagents.

EXPERIMENTAL

γ -(2-Phenanthryl)- β -methylbutyric acid.—A mixture of 2 g. of β -(2-phenanthroyl)-butyric acid (I), 5 g. of amalgamated zinc, 7.5 cc. of acetic acid, 7.5 cc. of concentrated hydrochloric acid, and 4 cc. of toluene was refluxed for thirty six hours. An additional 10 cc. of concentrated hydrochloric acid was added in portions over this time. The toluene layer was separated, the toluene was evaporated, and the oily residue was sublimed at 250° and 0.4 mm. The sublimate was crystallized from benzene-petroleum ether (b. p. 60–75°), as fine colorless prisms; weight, 0.96 g. (50%); m. p. 120–125°. After two further crystallizations from benzene-petroleum ether the melting point was raised to 127.5–129°.

Anal. Calc'd for $C_{19}H_{18}O_2$: C, 82.0; H, 6.5.

Found: C, 82.3; H, 6.7.

2-Methyl-4-keto-1,2,3,4-tetrahydrochrysene (II).—Four-tenths gram of γ -(2-phenanthryl)- β -methylbutyric acid was suspended in a mixture of 5 cc. of absolute ether and 1 drop of pyridine. When 1 cc. of thionyl chloride was added, the acid rapidly went into solution. After the solution had stood for a half-hour at room temperature, the ether and thionyl chloride were removed under reduced pressure. The acid chloride was dissolved in 5 cc. of dry benzene, the solution was cooled to 0°, and 0.75 cc. of stannic chloride was then added with swirling. After standing for fifteen minutes in the cold, the complex was hydrolyzed with ice and dilute hydrochloric acid. The benzene layer was washed with water, dilute ammonium hydroxide, and again with water. The benzene was evaporated, and the keto compound was crystallized from alcohol-acetone; weight, 0.32 g. (86%); m. p. 129–133°. After two recrystallizations from benzene-petroleum ether the melting point was 141–142°.

Anal. Calc'd for $C_{19}H_{16}O$: C, 87.7; H, 6.2.

Found: C, 87.3; H, 6.2.

2-Methyl-1,2,3,4-tetrahydrochrysene (III).—A mixture of 0.23 g. of 2-methyl-4-keto-1,2,3,4-tetrahydrochrysene, 5 g. of amalgamated zinc, 7.5 cc. of acetic acid, 7.5 cc. of concentrated hydrochloric acid, and 2 cc. of toluene was refluxed for twenty-four hours. The toluene layer was separated, the toluene was evaporated, and the residue was sublimed at 200° and 0.4 mm.; weight 0.18 g. (83%); m. p. 137–140°. After two crystallizations from acetone-alcohol the hydrocarbon melted at 141.5–142°. It first comes down as very thin leaflets which turn to thin prisms on standing in contact with the mother liquor. Both forms appear to have the same melting point.

Anal. Calc'd for $C_{19}H_{18}$: C, 92.7; H, 7.3.

Found: C, 92.3; H, 7.3.

The *hemi-picrate* crystallizes from alcohol-acetone as reddish-orange needles; m. p. 145–5–146°.

Anal. Calc'd for $2C_{19}H_{18} \cdot C_6H_5N_3O_7$: N, 5.8. Found: N, 6.0.

2-Methylchrysene (IV).—A mixture of 0.18 g. of 2-methyl-1,2,3,4-tetrahydrochrysene and 0.03 g. of palladium-charcoal catalyst⁸ was heated at 300–320° for one hour. The mixture was taken up in hot benzene and filtered. The benzene was evaporated, and the residue was crystallized from alcohol-acetone; weight, 0.16 g. (90%); m. p. 224–225°. Two further crystallizations gave colorless leaflets from benzene-alcohol; m. p. 224.5–225.5° (229–230° corr.).

Anal. Calc'd for $C_{19}H_{14}$: C, 94.2; H, 5.8.

Found: C, 94.5; H, 5.9.

The rather unstable *picrate* crystallizes from alcohol in the form of golden-yellow needles; m. p. 143–146°.

Anal. Calc'd for $C_{19}H_{14} \cdot C_6H_3N_3O_7$: N, 8.9. Found: N, 9.1.

2-n-Propylphenanthrene.—A mixture of 2 g. of 2-propionylphenanthrene, 4 g. of amalgamated zinc, 6 cc. of acetic acid, 6 cc. of concentrated hydrochloric acid, and 4 cc. of toluene was refluxed for twenty-four hours. An additional 5 cc. of concentrated hydrochloric acid was added over that time. The toluene layer was separated, and the toluene was evaporated. The oily residue, which did not crystallize, was dissolved in alcohol, and 3 g. of picric acid was added. On cooling, 3.2 g. of 2-n-propylphenanthrene *picrate* deposited; yield, 83%; m. p. 84–88°. The *picrate* was recrystallized twice from alcohol and then decomposed with dilute sodium hydroxide solution. The oil formed was taken up in benzene, the benzene layer was separated, the benzene was evaporated, and the residue was sublimed. The sublimate crystallized from alcohol-acetone in colorless leaflets; m. p. 35–36°.

Anal. Calc'd for $C_{17}H_{16}$: C, 92.7; H, 7.3.

Found: C, 92.6; H, 7.4.

The *picrate* crystallizes from alcohol in yellow needles; m. p. 92–93°.

Anal. Calc'd for $C_{17}H_{16} \cdot C_6H_3N_3O_7$: N, 9.4. Found: N, 9.4.

3-n-Propylphenanthrene.—Two grams of 3-propionylphenanthrene was reduced and worked up in the same way as the 2-propionylphenanthrene; weight of *picrate*, 2.98 g. (77%); m. p. 104–107°. By hydrolysis of the pure *picrate*, the 3-n-propylphenanthrene was obtained as a colorless oil which failed to crystallize, even when cooled to a low temperature.

Anal. Calc'd for $C_{17}H_{16}$: C, 92.7; H, 7.3.

Found: C, 93.1; H, 7.4.

The *picrate* crystallizes from alcohol as clusters of orange needles; m. p. 107–108°.

Anal. Calc'd for $C_{17}H_{16} \cdot C_6H_3N_3O_7$: N, 9.4. Found: N, 9.5.

γ -[2-(9,10-Dihydrophenanthryl)] butyric acid (V).—A mixture of 48 g. of β -[2-(9,10-dihydrophenanthryl)] propionic acid, 100 g. of amalgamated zinc, 150 cc. of acetic acid, 150 cc. of concentrated hydrochloric acid, and 80 cc. of toluene was refluxed for twenty hours. An additional 100 cc. of concentrated hydrochloric acid was added in portions over this time. The toluene layer was separated, the toluene was evaporated, and the residue was distilled in a vacuum. The distillate crystallized from dilute alcohol in colorless needles; yield, 42 g. (92%); m. p. 91–92°. This yield is somewhat higher than that reported by Burger and Mosettig⁴ who employed slightly different conditions.

γ -(2-Phenanthryl)butyric acid.—A stream of dry hydrogen chloride gas was passed into an ice-cold solution of 10 g. of γ -[2-(9,10-dihydrophenanthryl)] butyric acid in 300 cc. of methanol for a half hour. The solution was refluxed for an hour, and dry hydrogen chloride was again passed in the cooled solution for a half hour. After refluxing the solution again for an hour, most of the methanol was distilled, and

⁸ ZELINSKY AND TUROWA-POLLAK, *ibid.*, 58, 1295 (1925).

benzene was added. The benzene solution of the methyl ester was washed twice with water, and the benzene was distilled. The oily residue was dehydrogenated with 1 g. of palladium-charcoal catalyst at 240–260° for two hours. The mixture was taken up in benzene, and the catalyst was removed by filtration. The benzene was evaporated, and the ester was hydrolyzed with hot 40% potassium hydroxide solution. The hydrolysis mixture was diluted and acidified with concentrated hydrochloric acid. The precipitated acid was collected by filtration and crystallized from benzene as colorless plates; weight, 9.0–9.5 g. (90–95%, based on the dihydro acid); m. p. 133–134°. Haworth and Mavin³ report the melting point of this acid to be 134–135°. The recovered catalyst can be used for the dehydrogenation of a second run of ester with no apparent decrease in activity.

4-Keto-1,2,3,4-tetrahydrochrysene (VI).—To a suspension of 13.5 g. of γ -(2-phenanthryl)butyric acid in 100 cc. of dry ether and 5 drops of pyridine was added 30 cc. of thionyl chloride. The mixture was swirled until the acid had gone into solution, and was then allowed to stand at room temperature for a half-hour. The ether and thionyl chloride were evaporated under reduced pressure, and the acid chloride was dissolved in 100 cc. of benzene. The benzene solution was cooled to 0° and 22 cc. of stannic chloride was added with swirling. After standing for fifteen minutes in the cold, the complex was decomposed with ice and dilute hydrochloric acid. The benzene layer was washed with water, dilute ammonium hydroxide, and again with water. The benzene was evaporated, and the keto compound was crystallized from alcohol as light tan prisms; yield, 9.36 g. (74%); m. p. 122–124°. After two crystallizations and treatment with activated alumina, colorless prisms, m. p. 125–126°, were obtained. Haworth and Mavin³ report the melting point of this compound as 124–125°.

4-Methyl-4-hydroxy-1,2,3,4-tetrahydrochrysene (VII).—To a Grignard reagent made from 0.25 g. of magnesium, 0.75 cc. of methyl iodide, and 10 cc. of absolute ether were added 1 g. of 4-keto-1,2,3,4-tetrahydrochrysene and 10 cc. of dry benzene. The mixture was allowed to stand in the cold for twelve hours and was then decomposed with ice and ammonium chloride solution. The benzene-ether layer was separated, filtered, and then allowed to evaporate in an evaporating dish at room temperature. The methyl carbinol crystallized upon evaporation of the solvent as colorless prisms; weight, 0.87 g. (82%); m. p. 123.5–125°. After two recrystallizations from benzene-petroleum ether, the carbinol melted at 124–125°.

Anal. Calc'd for $C_{19}H_{18}O$: C, 87.0; H, 6.9.

Found: C, 87.5; H, 7.0.

4-Methylchrysene (VIII).—Six-tenths gram of 4-methyl-4-hydroxy-1,2,3,4-tetrahydrochrysene was heated with 0.06 g. of palladium-charcoal catalyst at 300–320° for one hour. The mixture was taken up in hot benzene and filtered. The hydrocarbon obtained from the residue crystallized from benzene-petroleum ether as colorless leaflets; weight, 0.51 g. (92%); m. p. 146–148°. After two recrystallizations from benzene-petroleum ether the melting point was 149–149.5° (151–151.5° corr.).

Anal. Calc'd for $C_{19}H_{14}$: C, 94.2; H, 5.8.

Found: C, 94.0; H, 5.6.

The *picrate* crystallizes from alcohol as bright-red needles; m. p. 134–135°.

Anal. Calc'd for $C_{19}H_{14} \cdot C_6H_5N_3O_7$: N, 8.9. Found: N, 9.0.

4-Hydroxy-1,2,3,4-tetrahydrochrysene (IX).—A solution of aluminum isopropoxide was prepared by refluxing a mixture of 1 g. of aluminum wire, 25 cc. of dry isopropyl alcohol, 5 drops of carbon tetrachloride, and a pinch of mercuric chloride. After the aluminum had dissolved, the isopropyl alcohol was distilled, and 2.75 g. of 4-keto-

1,2,3,4-tetrahydrochrysene and 25 cc. of toluene were added. The mixture was refluxed for four hours, 25 cc. of isopropyl alcohol was added and then distilled from the mixture. The toluene solution was cooled, and the aluminum salt was decomposed with cold 10% sulfuric acid. The toluene layer was separated, washed with dilute ammonium hydroxide, and evaporated in the cold. The carbinol separates as colorless silky needles; yield, 2.10 g. (76%); m. p. 156–158°. Two recrystallizations from benzene-petroleum ether raised the melting point to 160–162°. The carbinol gives a black color with sulfuric acid.

Anal. Calc'd for $C_{18}H_{16}O$: C, 87.1; H, 6.5.

Found: C, 87.5; H, 6.3.

4-Methoxy-1,2,3,4-tetrahydrochrysene.—To a solution of 0.05 cc. of concentrated sulfuric acid in 5 cc. of methanol was added 0.3 g. of 4-hydroxy-1,2,3,4-tetrahydrochrysene. The mixture was shaken occasionally, and after about a half-hour all the carbinol had gone into solution. The solution was allowed to stand overnight, then poured into a mixture of benzene and aqueous sodium carbonate. The benzene layer was separated, washed with water, filtered, and evaporated. The methyl ether crystallizes from methanol in colorless rhombic prisms; weight, 0.27 g. (86%); m. p. 79–80.5°.

Anal. Calc'd for $C_{19}H_{18}O$: C, 87.0; H, 6.9.

Found: C, 87.0; H, 6.8.

4-Acetoxy-1,2,3,4-tetrahydrochrysene.—Three-tenths gram of 4-hydroxy-1,2,3,4-tetrahydrochrysene was added to a solution of 0.3 cc. of pyridine and 0.6 cc. of acetic anhydride, and the mixture was heated on a steam bath for one hour. The acetic anhydride and the pyridine were then evaporated on a steam bath in a current of air, and the residue was dissolved in benzene. The benzene solution was washed with dilute ammonium hydroxide, water, dilute hydrochloric acid, and again with water. The acetate obtained from the benzene solution crystallized from petroleum ether in leaflets; yield, 0.30 g. (86%); m. p. 119–120.5°.

Anal. Calc'd for $C_{18}H_{20}O_2$: C, 82.8; H, 6.2.

Found: C, 83.2; H, 6.4.

4-Chloro-1,2,3,4-tetrahydrochrysene (X).—A stream of dry hydrogen chloride gas was passed into a cold solution of 0.2 g. of 4-hydroxy-1,2,3,4-tetrahydrochrysene in 10 cc. of dry benzene with 0.5 g. of calcium chloride suspended in it. The mixture turned cloudy almost immediately. After hydrogen chloride had been passed in for ten minutes the mixture was allowed to stand at room temperature for one hour, by which time the solution had again become clear. Evaporation of the benzene left a crystalline residue of the chloride. The latter crystallizes from benzene-petroleum ether in colorless, diamond-shaped prisms; yield, 0.17 g. (80%); it melts at 115–117° with decomposition, evolving hydrogen chloride. The melt solidifies and remelts at 174–178°.

Anal. Calc'd for $C_{18}H_{15}Cl$: Cl, 13.3. Found: Cl, 13.1.

1,2-Dihydrochrysene (XI).—A solution of 0.1 g. of 4-chloro-1,2,3,4-tetrahydrochrysene and 3 cc. of pyridine was refluxed for fifteen minutes; benzene and dilute hydrochloric acid were then added. The benzene solution was separated, washed with water, and the benzene was evaporated. The residue was sublimed at 200° and 0.4 mm. pressure; weight, 0.05 g. (58%); m. p. 181.5–183.5°. After two crystallizations from benzene-petroleum ether the colorless plates which were obtained melted at 182.5–184.5°.

Anal. Calc'd for $C_{18}H_{14}$: C, 93.9; H, 6.1.

Found: C, 93.4; H, 6.3.

The *picrate* forms bright-red needles from alcohol-acetone; m. p. 155–156°.

Anal. Calc'd for $C_{13}H_{14} \cdot C_6H_3N_3O_7$: N, 9.1. Found: N, 9.2.

1,2,3,4-Tetrahydrochrysene.—A mixture of 1 g. of 4-keto-1,2,3,4-tetrahydrochrysene, 4 g. of amalgamated zinc, 7 cc. of acetic acid, 7 cc. of concentrated hydrochloric acid, and 3 cc. of toluene was refluxed for twenty-four hours. An additional 5 cc. of concentrated hydrochloric acid was added in portions over this period. The toluene layer was separated, and the toluene was evaporated. The residue was sublimed at 200° and 0.4 mm.; weight, 0.56 g. (60%); m. p. 173–178°. After two crystallizations from benzene-petroleum ether, the hydrocarbon formed colorless leaflets; m. p. 180.5–181.5°.

Anal. Calc'd for $C_{18}H_{18}$: C, 93.1; H, 6.9.

Found: C, 92.9; H, 6.8.

The *picrate* formed orange needles from benzene containing an excess of picric acid; m. p. 134–135.5°.

Anal. Calc'd for $C_{18}H_{18} \cdot C_6H_3N_3O_7$: N, 9.3. Found: N, 9.1.

Chrysene.—(a) *From dihydrochrysene.*—A mixture of 0.43 g. of dihydrochrysene and 0.05 g. of palladium-charcoal catalyst was heated in a nitrogen atmosphere at 300–320° for one hour. The chrysene was taken up in benzene, and the solution was filtered to remove the catalyst. The benzene was evaporated, and the residue was crystallized from benzene, giving colorless, glistening leaflets; weight, 0.4 g. (93%); m. p. 247–249°. The hydrocarbon was also identified by means of its quinone.

(b) *From tetrahydrochrysene.*—A mixture of 0.32 g. of 1,2,3,4-tetrahydrochrysene and 0.04 g. of palladium-charcoal catalyst was treated as in part a; colorless, glistening leaflets; weight, 0.28 g. (87%); m. p. 247–249°.

SUMMARY

A number of new chrysene derivatives have been prepared from phenanthrene.

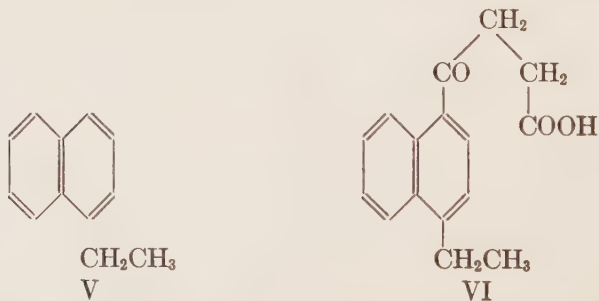
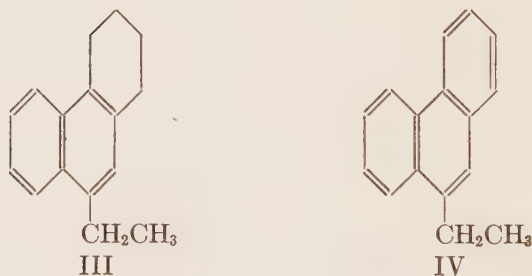
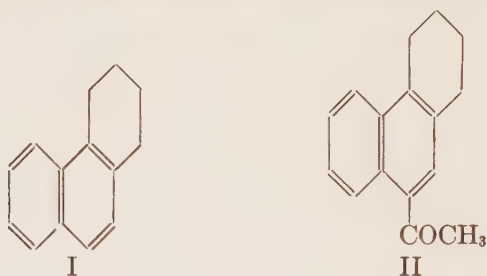
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UNIVERSITY OF MICHIGAN]

REACTIONS OF TETRAHYDROPHENANTHRENE. THE SYNTHESIS OF TRIPHENYLENE AND METHYLTRIPHENYLENE*

W. E. BACHMANN AND W. S. STRUVE

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In the Friedel-Crafts reaction phenanthrene is usually substituted in the 3 position and to a lesser extent in the 2 position. In order to obtain



* From the Ph.D. dissertation of W. S. Struve.

substituents in other positions, partially hydrogenated phenanthrene has been used. Although *as*-octahydrophenanthrene is attacked in the 3 position¹, the *sym*-octahydrophenanthrene can yield only 9-substituted derivatives in the Friedel-Crafts reaction². An excellent method of securing 2-substituted derivatives of phenanthrene exclusively in this reaction consists in the use of 9,10-dihydrophenanthrene^{3, 4}. We have undertaken a study of the reactions of 1,2,3,4-tetrahydrophenanthrene (I), and in this paper report the results obtained in the Friedel-Crafts reaction with acetyl chloride and with succinic anhydride. In the experimental section directions are given for the convenient preparation of tetrahydrophenanthrene from naphthalene, employing the Haworth method.

Acetyl chloride reacts with 1,2,3,4-tetrahydrophenanthrene in the 9 position to give 9-acetyltetrahydrophenanthrene (II). That the acetyl group was either in the 9 or the 10 position was shown by the formation of the known 9-acetylphenanthrene on dehydrogenation of the ketone by sulfur. Proof that the group is actually in the 9 position was obtained by reducing II by the Clemmensen method to 9-ethyl-1,2,3,4-tetrahydrophenanthrene (III), which proved to be identical with the compound prepared by a method which fixed the position of the ethyl group. In the latter synthesis, 1-ethylnaphthalene (V) was condensed with succinic anhydride; by analogy with the behavior of 1-methylnaphthalene, which reacts in the 4 position under the same conditions⁵, the product is probably VI. By the usual reduction, cyclization, and reduction of the cyclic ketone, 9-ethyltetrahydrophenanthrene (III) was obtained. The tetrahydro compound is smoothly dehydrogenated to 9-ethylphenanthrene (IV) by palladium on charcoal.

Tetrahydrophenanthrene reacts with succinic anhydride chiefly in the 9 position to give β -[9-(1,2,3,4-tetrahydrophenanthroyl)]propionic acid (VII); there was some evidence of the presence of an isomeric acid in the mixture, but this compound has not yet been obtained in a pure state. The structure of the acid was proved by its synthesis from 9-acetyltetrahydrophenanthrene (II), through the bromo ketone VIII, by means of the malonic ester synthesis.

By Clemmensen reduction of the tetrahydrophenanthroylpropionic acid (VII) the corresponding tetrahydrophenanthrylbutyric acid was obtained, and was cyclized, through its acid chloride, by stannic chloride to the ketoöctahydrotriphenylene (IX). Clemmensen reduction of this cyclic

¹ COOK AND HASLEWOOD, *J. Chem. Soc.*, **1935**, 767.

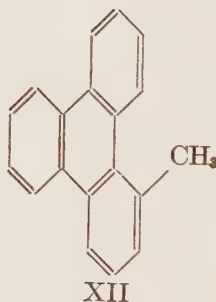
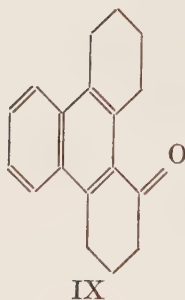
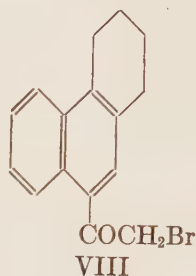
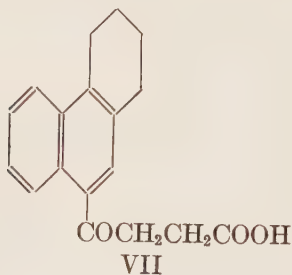
² VAN DE KAMP AND MOSETTIG, *J. Am. Chem. Soc.*, **57**, 1107 (1935).

³ BURGER AND MOSETTIG, *ibid.*, **57**, 2731 (1935).

⁴ BURGER AND MOSETTIG, *ibid.*, **59**, 1302 (1937).

⁵ HAWORTH AND MAVIN, *J. Chem. Soc.*, **1932**, 2720.

ketone yielded 1,2,3,4,5,6,7,8-octahydrotriphenylene (X), which was smoothly dehydrogenated to triphenylene by palladium on charcoal. Triphenylene has been synthesized recently by Bergmann and Blum-Bergmann⁶ from phenanthrene. By the action of methylmagnesium iodide on the cyclic ketone IX, the methyl carbinol was formed; the latter was converted to 1-methyltriphenylene (XII) by the action of the palladium-charcoal catalyst.



EXPERIMENTAL

γ-(1- and 2-Naphthyl)butyric acids.—In the manner prescribed by Haworth's directions,⁷ 52 g. of a mixture of β-(1- and 2-naphthoyl)propionic acids was obtained

⁶ BERGMANN AND BLUM-BERGMANN, *J. Am. Chem. Soc.*, **59**, 1441 (1937).

⁷ HAWORTH, *J. Chem. Soc.*, **1932**, 1125.

from 25 g. of succinic anhydride, 50 g. of naphthalene and 69 g. of aluminum chloride in 190 cc. of nitrobenzene. The mixture of acids, without recrystallization, was heated with 100 g. of amalgamated zinc, 75 cc. of water, 175 cc. of concentrated hydrochloric acid, 100 cc. of toluene and 5 cc. of acetic acid for twenty-four hours, an additional 150 cc. of concentrated hydrochloric acid being added in portions over this period. The toluene layer was separated, the toluene was evaporated, and the residue was distilled in a vacuum; yield, 38 g. (78%). The acids so obtained were used directly in the next step.

Mixture of 1- and 4-keto-1,2,3,4-tetrahydrophenanthrenes.—To a solution of 38 g. of a mixture of γ -(1- and 2-naphthyl)butyric acids in 200 cc. of absolute ether and 5 drops of pyridine was added 40 cc. of thionyl chloride. After standing at room temperature for a half hour the ether and thionyl chloride were evaporated under reduced pressure. The oily acid chloride was dissolved in 200 cc. of dry benzene and cooled in an ice bath. Then 30 cc. of stannic chloride was added, and the mixture allowed to stand in the ice water for fifteen minutes. The complex was hydrolyzed with ice and dilute hydrochloric acid, the benzene layer was separated, washed with water and dilute ammonium hydroxide solution, the benzene was evaporated, and the residue was distilled under reduced pressure (0.4 mm.), yielding a colorless liquid; weight, 26 g. (75%).

1,2,3,4-Tetrahydrophenanthrene (I).—Twenty-six grams of the mixture of 1- and 4-keto-1,2,3,4-tetrahydrophenanthrene, 100 g. of amalgamated zinc, 150 cc. of acetic acid, 150 cc. of concentrated hydrochloric acid, and 100 cc. of toluene was refluxed for twenty-four hours, an additional 75 cc. of concentrated hydrochloric acid being added in portions over this time. Vacuum distillation of the residue obtained from the toluene layer gave tetrahydrophenanthrene as a colorless liquid; yield, 16.5 g. (69%). In one run the distillate from 23 g. of starting material was dissolved in alcohol, and an excess of picric acid was added. The solution deposited 33 g. of picrate; m. p. 110–112°, corresponding to a 68 per cent. yield of tetrahydrophenanthrene. The melting point of pure tetrahydrophenanthrene picrate is 111°. The picrate was decomposed with dilute ammonium hydroxide, and the oil so obtained was crystallized from methanol, giving colorless plates; m. p. 32.5–33.5°. It is not necessary however to purify the tetrahydrophenanthrene through the picrate in order to crystallize it. In another run 26 g. of distillate from 37.5 g. of starting material was crystallized from methanol, giving about 22 g. of crystalline product; m. p. 32–33°. Because of the large solubility of the tetrahydrophenanthrene in methanol there is some loss upon crystallization and it has been found that either the liquid or solid tetrahydrophenanthrene can be used in the following experiments.

9-Acetyl-1,2,3,4-tetrahydrophenanthrene (II).—To a solution of 13.5 g. of aluminum chloride and 4.5 g. of acetyl chloride in 42 cc. of dinitrobenzene cooled to -10° was added 10 g. of 1,2,3,4-tetrahydrophenanthrene. The mixture was kept in a refrigerator for twenty-four hours. After two hours the reaction mixture had solidified. The mixture was hydrolyzed with ice and dilute hydrochloric acid, the solution was washed with water, and the nitrobenzene was removed by steam distillation. The residue crystallized on cooling; yield, 11.7 g. (95%); m. p. 45–50°. The crude mixture was distilled in a vacuum, giving 10.5 g. of distillate, which crystallized from methanol-alcohol as slightly yellow prisms; weight, 7.9 g. (75% of the distilled product); m. p. 56–58°. The second crop (1.33 g.) melted at 40–52°. Two recrystallizations of the first crop from alcohol-methanol gave colorless prisms of 9-acetyl-1,2,3,4-tetrahydrophenanthrene; m. p. 56.5–58°.

⁸ SCHROETER, MÜLLER, AND HUANG, *Ber.*, **62B**, 653 (1929).

Anal. Calc'd for $C_{16}H_{16}O$: C, 85.7; H, 7.1.

Found: C, 86.0; H, 7.1.

9-Acetylphenanthrene.—A mixture of 0.5 g. of 9-acetyl-1,2,3,4-tetrahydrophenanthrene and 0.17 g. of sulfur was heated for three hours at 210–220°. A small amount of powdered copper was then added, and the heating was continued for ten minutes more. The mixture was extracted with benzene, the benzene solution was filtered, and the benzene was evaporated. The residue was sublimed at 220° and 0.4 mm., and the sublimate was crystallized from alcohol; yield, 0.22 g. (46%); m. p. 70–73°. The melting point of a mixture with authentic 9-acetylphenanthrene (m. p. 72.5–73°) prepared from 9-cyanophenanthrene and methylmagnesium iodide⁹ was 71–73°.

β -[1-(4-Ethyl-naphthoyl)]propionic acid (VI).—To a cold solution of 3.5 g. of succinic anhydride and 8.5 g. of anhydrous aluminum chloride in 27 cc. of nitrobenzene was added 5.4 g. of 1-ethylnaphthalene (V), and the mixture was kept at 0° for fifteen hours. The complex was hydrolyzed with ice and dilute hydrochloric acid, the nitrobenzene solution was washed with water, and the nitrobenzene was removed by steam distillation. The residue was dissolved in a solution of 5 g. of sodium hydroxide in 200 cc. of water, the solution treated with charcoal, filtered, and acidified. The precipitated acid weighed 6.5 g. (74%); m. p. 122–127°. Crystallization from benzene gave colorless needles; m. p. 127–131°; two further crystallizations from benzene raised the melting point to 129.5–131°.

Anal. Calc'd for $C_{16}H_{16}O_3$: C, 75.0; H, 6.3.

Found: C, 74.8; H, 6.2.

γ -[1-(4-Ethyl-naphthyl)]butyric acid.—A mixture of 4 g. of β -[1-(4-ethylnaphthoyl)]propionic acid, 10 g. of amalgamated zinc, 15 cc. of acetic acid, 15 cc. of concentrated hydrochloric acid, and 8 cc. of toluene was refluxed for twenty-four hours. An additional 15 cc. of concentrated hydrochloric acid was added in portions over this period. The toluene layer was separated, the toluene was evaporated, and the residue was crystallized from benzene; weight, 3.54 g. (94%); m. p. 113–116°. Two further crystallizations from benzene gave clusters of colorless needles; m. p. 115–116.5°.

Anal. Calc'd for $C_{16}H_{16}O_2$: C, 79.3; H, 7.4.

Found: C, 79.2; H, 7.4.

1-Keto-9-ethyl-1,2,3,4-tetrahydrophenanthrene.—To a solution of 2 g. of γ -[1-(4-ethylnaphthyl)]butyric acid in 20 cc. of absolute ether and 5 drops of pyridine was added 4 cc. of thionyl chloride. The mixture was allowed to stand at room temperature for a half-hour, and then the ether and thionyl chloride were removed under reduced pressure. An ice-cold solution of the acid chloride in 20 cc. of benzene was treated with 3 cc. of stannic chloride, and the solution was kept cold for a half-hour. The complex was hydrolyzed with ice and dilute hydrochloric acid, the benzene layer was separated, washed with water and dilute ammonium hydroxide, and the benzene was evaporated. The residue crystallized from dilute alcohol as colorless needles; yield, 1.42 g. (77%); m. p. 51–53°. Two further crystallizations raised the melting point to 52–53°.

Anal. Calc'd for $C_{16}H_{16}O$: C, 85.7; H, 7.1.

Found: C, 85.3; H, 7.3.

9-Ethyl-1,2,3,4-tetrahydrophenanthrene (III).—(a) *From 9-acetyl-1,2,3,4-tetrahydrophenanthrene.*—A mixture of 1 g. of 9-acetyl-1,2,3,4-tetrahydrophenanthrene, 5 g. of amalgamated zinc, 10 cc. of acetic acid, 10 cc. of concentrated hydrochloric acid, and 4 cc. of toluene was refluxed for twenty-four hours, an additional 6 cc. of

⁹ BACHMANN AND BOATNER, *J. Am. Chem. Soc.*, **58**, 2098 (1936).

concentrated hydrochloric acid being added in portions over this period. The toluene layer was separated, the toluene was evaporated, and the residue was sublimed at 200° and 0.4 mm. The sublimate was crystallized from alcohol-acetone; weight, 0.51 g.; m. p. 22–24°. To the filtrate from the crystallization was added 0.7 g. of picric acid. A bright orange picrate crystallized; weight, 0.64 g.; m. p. 124–126°. Total yield, 0.82 g. (88%).

(b) *From 1-keto-9-ethyl-1,2,3,4-tetrahydrophenanthrene*.—One gram of this ketone was reduced in exactly the same way as the 9-acetyl-1,2,3,4-tetrahydrophenanthrene; weight, 0.27 g.; m. p. 23–25°. The melting point of a mixture with the material obtained in part *a* was 22–24.5°. The picrate obtained from the filtrate from the crystallization weighed 0.84 g.; m. p. 124–126°. The melting point of a mixture with the picrate obtained in part *a* was 124–126°.

After two recrystallizations of the hydrocarbon from alcohol-acetone, colorless needles with unchanged melting point were obtained.

Anal. Calc'd for $C_{16}H_{18}$: C, 91.4; H, 8.6.

Found: C, 91.3; H, 8.8.

The pure picrate crystallizes from alcohol as clusters of fine, bright-orange needles; m. p. 125.5–126.5°.

Anal. Calc'd for $C_{16}H_{18} \cdot C_6H_3N_3O_7$: N, 9.6. Found: N, 9.7.

9-Ethylphenanthrene (IV).—A mixture of 0.27 g. of 9-ethyl-1,2,3,4-tetrahydrophenanthrene and 0.04 g. of palladium-charcoal catalyst¹⁰ was heated for one hour at 300–320°. The mixture was taken up in benzene, the solution was filtered to remove the catalyst, the benzene was evaporated, and the residue was crystallized from alcohol, giving colorless needles; weight, 0.20 g. (75%); m. p. 63.5–64.5°. The picrate melted at 120.5–122.5°. Mosettig and van de Kamp¹¹ give 62.5–63° and 123–124° for the melting points of the hydrocarbon and the picrate respectively.

ω -Bromo-9-acetyl-1,2,3,4-tetrahydrophenanthrene (VIII).—A solution of 1.48 g. of bromine in 40 cc. of absolute ether was added to a solution of 2 g. of 9-acetyl-1,2,3,4-tetrahydrophenanthrene in 80 cc. of absolute ether cooled in an ice-salt mixture. An orange precipitate formed which dissolved as the solution decolorized, the decolorization taking twenty minutes. After standing another half hour the ether was evaporated, and the residue was crystallized from methanol; yield, 1.95 g. (72%); m. p. 90–91°. Two further crystallizations from methanol gave colorless needles; m. p. 90.5–91.5°.

Anal. Calc'd for $C_{16}H_{15}BrO$: Br, 26.4. Found: Br, 26.3.

β -[9-(1,2,3,4-Tetrahydrophenanthroyl)]propionic acid (VII).—(a) A mixture of 0.05 g. of sodium, 0.5 cc. of malonic ester, and 10 cc. of benzene was refluxed for twelve hours, 0.39 g. of ω -bromo-9-acetyl-1,2,3,4-tetrahydrophenanthrene was then added, and the whole was refluxed for twenty-four hours. The benzene solution was washed with cold dilute hydrochloric acid, and the benzene was evaporated. The residue was heated with 3 cc. of 40% potassium hydroxide solution for a half-hour, water was added to dissolve the potassium salts formed, and the solution was filtered and acidified. The dry dicarboxylic acid was heated at 160–180° for a half-hour. It was then taken up in benzene, the acid was extracted with dilute potassium hydroxide, and the solution of the potassium salt was filtered. Acidification gave 0.24 g. (66%) of the desired acid; m. p. 160–163°. Two crystallizations from acetic acid gave colorless rectangular prisms; m. p. 167–169°.

(b) To a cooled solution of 2.2 g. of succinic anhydride and 5.4 g. of aluminum

¹⁰ ZELINSKY AND TUROWA-POLLAK, *Ber.*, **58**, 1295 (1925).

¹¹ MOSETTIG AND VAN DE KAMP, *J. Am. Chem. Soc.*, **55**, 3442 (1933).

chloride in 17 cc. of nitrobenzene was added 4 g. of tetrahydrophenanthrene. The mixture was kept cold for twelve hours, and was then hydrolyzed with ice and dilute hydrochloric acid. The nitrobenzene solution was washed with water, steam distilled to remove the nitrobenzene, and the residue was dissolved in hot dilute sodium hydroxide solution. Acidification of the filtered solution gave 4.83 g. (78%) of the acids; m. p. 137–155°. After one recrystallization from benzene-petroleum ether, 3.32 g. of acid melting at 161–165° was obtained. After two further recrystallizations from toluene-acetic acid the acid was obtained as colorless, rectangular prisms; m. p. 167.5–169°, alone and when mixed with the acid prepared in part *a*.

Anal. Calc'd for $C_{18}H_{18}O_3$: C, 76.6; H, 6.4.

Found: C, 76.7; H, 6.5.

γ -[9-(1,2,3,4-Tetrahydrophenanthryl)]butyric acid.—A mixture of 1.49 g. of β -[9-(1,2,3,4-tetrahydrophenanthroyl)]propionic acid, 3.0 g. of amalgamated zinc, 4.8 cc. of acetic acid, 4.8 cc. of concentrated hydrochloric acid, and 2 cc. of toluene was refluxed for twenty-four hours, an additional 5 cc. of concentrated hydrochloric acid being added over this time. The toluene layer was separated, the toluene was evaporated, and the residue was crystallized from benzene; yield, 1.37 g. (96%); m. p. 132.5–134°. After two recrystallizations it separated as colorless prisms; m. p. 133–134°.

Anal. Calc'd for $C_{18}H_{20}O_2$: C, 80.6; H, 7.5.

Found: C, 81.1; H, 7.6.

γ -(9-Phenanthryl)butyric acid.—A mixture of the methyl ester obtained from 1 g. of γ -[9-(1,2,3,4-tetrahydrophenanthryl)]butyric acid by means of diazomethane and 0.1 g. of palladium-charcoal catalyst was heated for two hours at 250–270°. The mixture was taken up in benzene, and the catalyst was removed by filtration. The benzene was evaporated, and the ester was hydrolyzed with hot 40% potassium hydroxide solution. Acidification of the diluted hydrolysis mixture gave 0.89 g. (90%) of the acid; m. p. 167–170°. After two crystallizations from benzene the acid gave colorless needles; m. p. 171–172°. Bergmann and Blum-Bergmann⁶ give 176° for the melting point of γ -(9-phenanthryl)butyric acid, which they prepared by reduction of the keto acid obtained by interaction of 9-phenanthrylmagnesium bromide and succinic anhydride.

1-Keto-1,2,3,4,9,10,11,12-octahydrotriphenylene (IX).—To a solution of 1.55 g. of γ -[9-(1,2,3,4-tetrahydrophenanthryl)]butyric acid in 15 cc. of absolute ether and 5 drops of pyridine was added 3 cc. of thionyl chloride. The solution was allowed to stand for a half-hour, and the ether and thionyl chloride were then evaporated under reduced pressure. The acid chloride was dissolved in 15 cc. of dry benzene, the solution was cooled in ice water, and 2.5 cc. of stannic chloride was added with swirling. The mixture was allowed to stand for ten minutes in the cold, and then the complex was decomposed with ice and dilute hydrochloric acid. The benzene layer was washed with dilute ammonium hydroxide, the benzene was evaporated, and the residue was crystallized from alcohol-acetone; weight, 1.37 g. (95%); m. p. 121–121.5°. After two recrystallizations from alcohol-acetone, the compound formed colorless needles; m. p. 121–122°.

Anal. Calc'd for $C_{18}H_{18}O$: C, 86.4; H, 7.2.

Found: C, 86.5; H, 7.1.

1,2,3,4,5,6,7,8-octahydrotriphenylene (X).—A mixture of 0.78 g. of the aforementioned cyclic ketone, 3 g. of amalgamated zinc, 5 cc. of acetic acid, 5 cc. of concentrated hydrochloric acid and 2 cc. of toluene was refluxed for twenty-four hours; an additional 5 cc. of concentrated hydrochloric acid was added over this period.

The product obtained from the toluene layer was sublimed at 200° and 0.4 mm., and the sublimate was crystallized from alcohol-acetone; yield, 0.54 g. (74%); m. p. $117.5-119.5^{\circ}$. Two further crystallizations gave colorless prisms; m. p. $120.5-122^{\circ}$.

Anal. Calc'd for $C_{18}H_{20}$: C, 91.5; H, 8.5.

Found: C, 91.3; H, 8.3.

The *picrate* crystallizes from alcohol-acetone as red needles; m. p. $193-195^{\circ}$.

Anal. Calc'd for $C_{18}H_{20} \cdot C_6H_3N_3O_7$: N, 9.0. Found: N, 9.0.

Triphenylene (XI).—A mixture of 0.13 g. of the octahydrotriphenylene and 0.02 g. of palladium-charcoal catalyst was heated for one hour at $300-320^{\circ}$. The mixture was taken up in benzene, and filtered to remove the catalyst; the benzene was evaporated, and the residue was crystallized from acetone-alcohol, giving colorless needles; yield, 0.095 g. (75%); m. p. $196.5-197.5^{\circ}$. The compound gave no depression of melting point when mixed with authentic triphenylene. The mixture melting point of the picrates also gave no depression.

1-Methyl-1-hydroxy-1,2,3,4,9,10,11,12-octahydrotriphenylene.—An ice-cold solution of a Grignard reagent made from 0.56 cc. of methyl iodide, 0.19 g. of magnesium, and 10 cc. of ether was treated with a cold solution of 0.75 g. of 1-keto-1,2,3,4,9,10,11,12-octahydrotriphenylene in 10 cc. of dry benzene. The mixture was allowed to stand in the cold overnight, and then hydrolyzed with ice and dilute ammonium chloride solution. Evaporation of the benzene-ether layer in an open vessel gave colorless crystals of the methyl carbinol; yield, 0.43 g. (54%); m. p. $102-105^{\circ}$. After two crystallizations from benzene-petroleum ether the methyl carbinol melted at $104-105^{\circ}$.

Anal. Calc'd for $C_{19}H_{22}O$: C, 85.7; H, 8.3.

Found: C, 85.5; H, 8.5.

1-Methyltriphenylene (XII).—A mixture of 0.43 g. of the aforementioned carbinol and 0.05 g. of palladium charcoal catalyst was heated for two hours at $300-320^{\circ}$. The mixture was taken up in benzene, filtered, and the benzene was evaporated. The residue crystallized from alcohol-acetone in the form of colorless needles; yield, 0.35 g. (90%); m. p. $89-90^{\circ}$. Two recrystallizations raised the melting point to $93-94^{\circ}$.

Anal. Calc'd for $C_{19}H_{14}$: C, 94.2; H, 5.8.

Found: C, 94.2; H, 5.8.

The *picrate* crystallizes from alcohol as golden-yellow needles; m. p. $172.5-174^{\circ}$.

Anal. Calc'd for $C_{19}H_{14} \cdot C_6H_3N_3O_7$: N, 8.9. Found: N, 9.0.

SUMMARY

The reactions of 1,2,3,4-tetrahydrophenanthrene with succinic anhydride and with acetyl chloride have been investigated. In both cases the substituent group enters the 9 position of the tetrahydrophenanthrene.

The syntheses of triphenylene and of 1-methyltriphenylene are described.

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE SYNTHESIS OF METHYLCHRYSENES AND RELATED COMPOUNDS¹

W. E. BACHMANN AND W. S. STRUVE

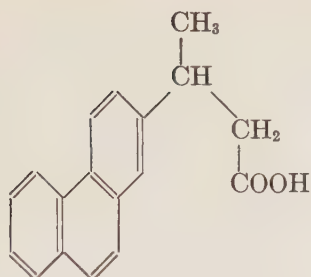
Received March 8, 1940

Only three of the six possible monomethylchrysenes have been synthesized. In a previous paper (1) we have reported the preparation of 2-methylchrysene and 4-methylchrysene. The latter isomer has also been synthesized independently by Fieser and Johnson (2), and 6-methylchrysene has been obtained by Newman (3). In this paper we are reporting the synthesis of 1-methylchrysene and 3-methylchrysene, each by two independent methods, as well as new procedures for obtaining 2-methylchrysene and 4-methylchrysene.

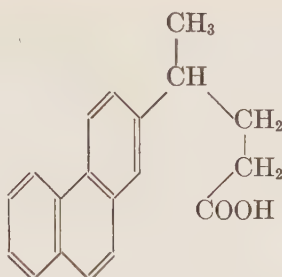
The starting material for the preparation of 1-methylchrysene (V) was 2-acetylphenanthrene, which can be obtained readily by acetylation of phenanthrene. This ketone was reduced to methyl-2-phenanthryl carbinol in excellent yield by means of aluminum isopropoxide (4). The bromide, obtained by interaction of the carbinol and phosphorus tri-bromide, was condensed with sodio-malonic ester, and the product was converted into β -(2-phenanthryl) butyric acid (I). The side chain of this acid was lengthened by means of the Arndt-Eistert reaction (5) and γ -(2-phenanthryl) valeric acid (II) was obtained in good yield. Cyclization of the acid chloride in carbon disulfide by stannic chloride yielded 1-methyl-4-keto-1,2,3,4-tetrahydrochrysene (III). Clemmensen reduction of this cyclic ketone gave 1-methyl-1,2,3,4-tetrahydrochrysene (IV), which was smoothly dehydrogenated to 1-methylchrysene (V) by palladium on charcoal. This hydrocarbon possesses properties which are quite different from those of 5-methyl-1,2-benzanthracene, which would have resulted if cyclization had occurred in the 3 position of the phenanthrene nucleus. Further proof of the structure of the compound was obtained by its synthesis by the method to be described.

By reaction of 1-methyl-4-ketotetrahydrochrysene (III) with methylmagnesium iodide, followed by dehydration and dehydrogenation of the product, 1,4-dimethylchrysene was prepared.

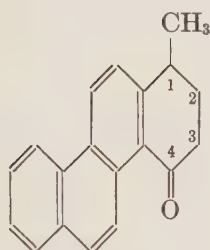
¹ From the Ph.D. dissertation of W. S. Struve.



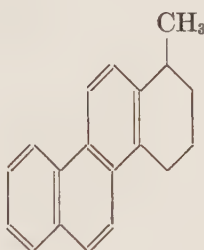
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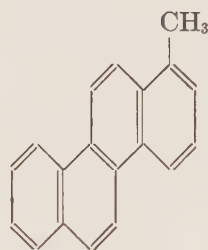
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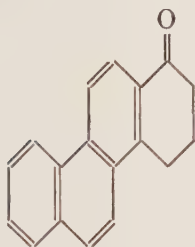
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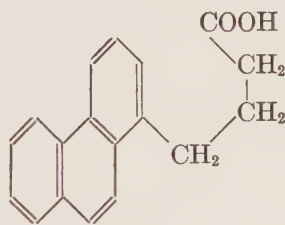
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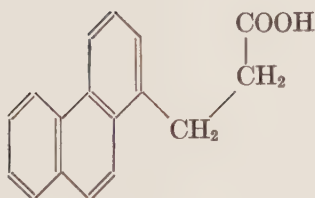
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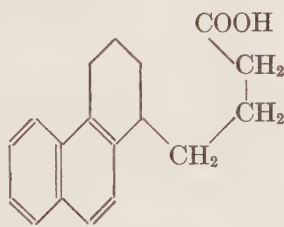
VI



VII



VIII

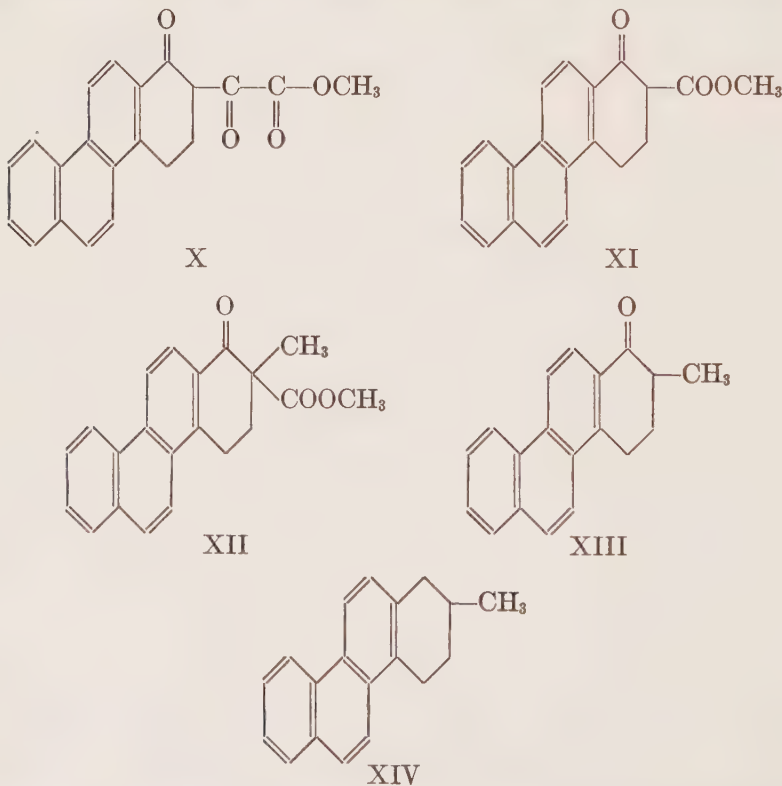


IX

In the second synthesis, 1-methylchrysene was obtained by dehydration and dehydrogenation of the carbinol formed by interaction of methylmagnesium iodide and 1-keto-1,2,3,4-tetrahydrochrysene (VI). The latter compound was first prepared by Hoch (6) by cyclization of γ -(1-phenanthryl)butyric acid (VII) by means of stannic chloride. We em-

ployed the acid chloride rather than the free acid for cyclization. The acid was obtained in two ways: from 1-keto-1,2,3,4-tetrahydrophenanthrene according to Hoch's procedure, and from β -(1-phenanthryl)propionic acid, which can be prepared readily from 1-phenanthraldehyde. In the first method we dehydrogenated the methyl ester of the intermediate γ -[1-(1,2,3,4-tetrahydrophenanthryl)]butyric acid (IX) by palladized charcoal in excellent yields, whereas Hoch used sulfur for this purpose. In the second method the Arndt-Eistert reaction was employed to convert the β -(1-phenanthryl)propionic acid (VIII) to γ -(1-phenanthryl)butyric acid. The products obtained by the two methods were identical. 1-Ethylchrysene was obtained by dehydration and dehydrogenation of the product formed by interaction of the 1-ketotetrahydrochrysene and ethylmagnesium bromide.

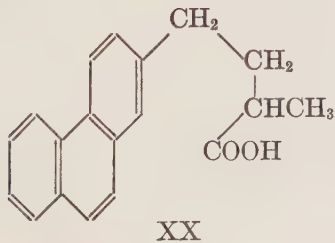
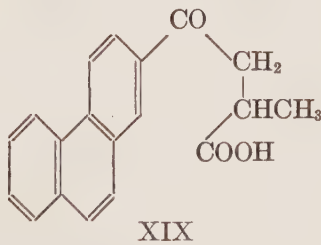
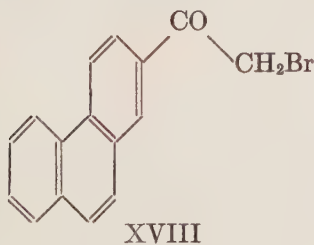
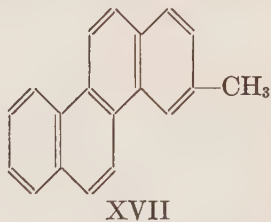
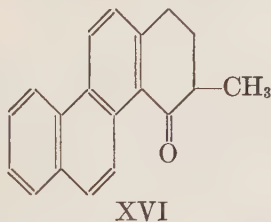
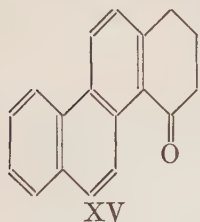
In order to prepare 2-methylchrysene, the 1-ketotetrahydrochrysene was condensed with methyl oxalate by means of sodium methoxide in an



atmosphere of nitrogen to give methyl 1-keto-1,2,3,4-tetrahydrochrysene-2-glyoxalate (X). The yield of glyoxalate was lower when the reac-

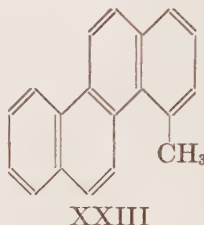
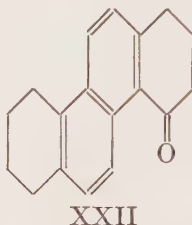
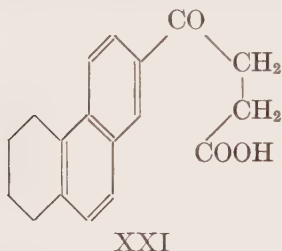
tion was carried out in air, presumably through the susceptibility of the sodio derivative to oxygen. The glyoxalate was smoothly converted to 1-keto-2-carbomethoxy-1,2,3,4-tetrahydrochrysene (XI) by loss of carbon monoxide when it was heated to 180–190° with powdered soft glass, the procedure recently developed by Bachmann, Cole, and Wilds (7). By treating the sodio derivative of this compound with methyl iodide, 1-keto-2-methyl-2-carbomethoxy-1,2,3,4-tetrahydrochrysene (XII) was obtained. The latter compound, on hydrolysis and subsequent decarboxylation, gave 1-keto-2-methyl-1,2,3,4-tetrahydrochrysene (XIII) in excellent yield. Clemmensen reduction of the ketone gave 2-methyl-1,2,3,4-tetrahydrochrysene (XIV), identical with that which had previously been made by a different method. The dehydrogenation of the compound to 2-methylchrysene was described in the previous paper (1).

In a similar manner, 4-keto-1,2,3,4-tetrahydrochrysene (XV) was condensed with methyl oxalate and the product converted to 3-methylchrysene (XVII) by the reactions just described. The intermediate 3-methyl-4-keto-1,2,3,4-tetrahydrochrysene (XVI) was also prepared from ω -bromo-2-acetylphenanthrene (XVIII). Condensation of this compound with sodio-methylmalonic ester, followed by hydrolysis and decarboxylation of the product of the reaction, gave β -(2-phenanthrolyl)- α -methyl-



propionic acid (XIX) in poor yield. Clemmensen reduction of the keto acid gave a good yield of γ -(2-phenanthryl)- α -methylbutyric acid (XX), which was cyclized through its acid chloride by stannic chloride to XVI.

In a previous paper (8) we reported that tetrahydrophenanthrene reacts with succinic anhydride chiefly in the 9 position to give β -[9-(1,2,3,4-tetrahydrophenanthroyl)]propionic acid, but there was some evidence of the formation of an isomeric acid. We have now succeeded in isolating the isomeric acid and have shown it to be β -[7-(1,2,3,4-tetrahydrophenanthroyl)]propionic acid (XXI). The structure of the acid followed from the formation of γ -(2-phenanthryl)butyric acid when the reduced acid (γ -[7-(1,2,3,4-tetrahydrophenanthryl)]butyric acid) was dehydrogenated (in the form of its methyl ester) by palladized charcoal. Cyclization of the γ -[7-(1,2,3,4-tetrahydrophenanthryl)]butyric acid through its acid chloride by stannic chloride gave 4-keto-1,2,3,4,7,8,9,10-octahydrochrysene



(XXII). From this compound 4-methylchrysene (XXIII) was obtained through the action of methylmagnesium iodide, followed by dehydration and dehydrogenation of the product. The formation of this product constitutes further proof of the structure of the keto acid and shows that ring closure took place from the 7 to the 8 position in the 1,2,3,4-tetrahydrophenanthrene molecule.

EXPERIMENTAL

All melting points are uncorrected.

Methyl-2-phenanthryl carbinol. To a solution of aluminum isopropoxide prepared by refluxing 10 g. of aluminum wire, 5 drops of carbon tetrachloride, a pinch of mercuric chloride, and 250 cc. of isopropyl alcohol was added 10 g. of 2-acetylphenanthrene (9) and 250 cc. of isopropyl alcohol. The mixture was refluxed for one hour, and then 250 cc. of isopropyl alcohol was distilled off over a period of two hours. The complex was decomposed with ice-cold 10% sulfuric acid, the carbinol was taken up in benzene, the benzene extract was washed with dilute ammonium hydroxide and then with water, and the benzene was evaporated at room temperature. The residue crystallized from benzene-petroleum ether; weight, 9.60 g. (95%); m.p. 131–131.5°. Mosettig and van de Kamp (10), who prepared the compound by catalytic hydrogenation of the ketone, give 134–135° as the melting point of the carbinol.

α -(2-Phenanthryl)ethyl bromide. To an ice-cold suspension of 10 g. of the above

carbinol in 70 cc. of dry ether was added 2.95 cc. of phosphorus tribromide. The mixture was allowed to stand for an hour in the cold, the ether was evaporated at room temperature, and the residue was triturated with a small amount of methanol, cooled, and filtered; weight, 11.47 g. (89%); m.p. 84–85.5°. For further purification the bromide was dissolved in benzene, the benzene solution was washed with dilute sodium bicarbonate solution, the benzene was evaporated at room temperature, and the residue was crystallized several times from benzene-petroleum ether, from which it was obtained as colorless leaflets; m.p. 86–88°.

Anal. Calc'd for $C_{16}H_{13}Br$: Br, 28.1. Found: Br, 28.5.

β -(2-Phenanthryl)butyric acid (I). To a solution of ethyl sodio-malonate prepared from 0.48 g. of sodium, 4.2 cc. of malonic ester, and 20 cc. of absolute alcohol was added 3.89 g. of purified 2-phenanthrylethyl bromide dissolved in 30 cc. of benzene. The solution was allowed to stand at room temperature overnight and was then refluxed for two hours. If the bromide is added to a hot suspension of sodio-malonic ester in benzene and the whole is refluxed for twelve hours, the yield of product is low. As much alcohol as possible was distilled off, benzene and dilute hydrochloric acid were added, the benzene layer was washed with water, the benzene was evaporated, and the residue was heated for an hour with 45% potassium hydroxide solution. The mixture was diluted to dissolve the potassium salt and acidified. The dicarboxylic acid was heated at 180° for a half hour, and the decarboxylated product was crystallized from chloroform-petroleum ether; weight, 3.14 g. (87%); m.p. 128–130°, resolidifying on further heating and remelting at 137–138°. After two recrystallizations from chloroform-petroleum ether and seeding with the high-melting form, the acid melted at 138–139°. It is not necessary to use purified bromide; in a run, using 5 g. of the crude bromide, 3.83 g. (83%) of acid softening at 129°, resolidifying on further heating and melting completely at 137.5–138.5°, was obtained. Bergmann and Hillemann (11), who prepared this acid by the Reformatsky reaction, give 125–127° as the melting point of this compound.

γ -(2-Phenanthryl)valeric acid (II). To a suspension of 1.32 g. of β -(2-phenanthryl)butyric acid in 2 cc. of dry ether and 1 drop of pyridine was added 1 cc. of thionyl chloride, and the mixture was allowed to stand at room temperature for a half hour. The ether and thionyl chloride were then evaporated under reduced pressure, the acid chloride was dissolved in ether, and was added drop by drop to a solution of diazomethane in 25 cc. of ether, the diazomethane being prepared from 3 cc. of ethyl N-methyl-N-nitrosocarbamate. After standing at room temperature for two hours, the ether was evaporated under reduced pressure and the oily diazo ketone was dissolved in 15 cc. of dry methanol. The methanol solution was refluxed for one hour, with addition of silver oxide from 2.5 cc. of 10% silver nitrate solution. Half of the silver oxide was added at the beginning of the heating and the rest in five portions at five minute intervals. The methanol solution was filtered and the residue from evaporation of the methanol was heated for an hour with 45% potassium hydroxide solution. The mixture was diluted to dissolve the potassium salts, filtered, and acidified; weight, 1.34 g.; m.p. 124–130°. The crude acid was sublimed at 230° and 0.4 mm. and the sublimate was crystallized from benzene-petroleum ether; weight, 1.15 g. (83%); m.p. 132–134°. After several further crystallizations from benzene-petroleum ether the acid was obtained as colorless leaflets; m.p. 136.5–138.5°.

Anal. Calc'd for $C_{16}H_{15}O_2$: C, 82.0; H, 6.5.

Found: C, 81.9; H, 6.5.

1-Methyl-4-keto-1,2,3,4-tetrahydrochrysene (III). To a suspension of 2.85 g. of γ -(2-phenanthryl)valeric acid in 30 cc. of ether and 2 drops of pyridine was added 6

cc. of thionyl chloride. After standing at room temperature for a half hour, the ether and thionyl chloride were removed under reduced pressure. The acid chloride was dissolved in 30 cc. of carbon disulfide (benzene proved less satisfactory) and 4.5 cc. of stannic chloride was added to the chilled solution. After standing at room temperature for one hour, the mixture was hydrolyzed with ice and hydrochloric acid, the carbon disulfide layer was washed with water, and the carbon disulfide was evaporated. The residue was dissolved in benzene, the benzene solution was washed with ammonium hydroxide and then with water, the benzene was evaporated, and the ketone was crystallized from acetone-alcohol; weight, 1.91 g. (72%); m.p. 94-96.5°. After two further crystallizations from alcohol-acetone, colorless prisms of the ketone were obtained; m.p. 98.5-99.5°. Sometimes on crystallization the ketone separates as leaflets which melt at 75-77° and can be changed to the higher-melting form by seeding with it.

Anal. Calc'd for $C_{19}H_{18}O$: C, 87.7; H, 6.2.

Found: C, 88.0; H, 6.1.

1-Methyl-1,2,3,4-tetrahydrochrysene (IV). A mixture of 1 g. of 1-methyl-4-keto-1,2,3,4-tetrahydrochrysene, 10 g. of amalgamated zinc, 20 cc. of acetic acid, 12 cc. of concentrated hydrochloric acid, and 5 cc. of toluene was refluxed for twenty-four hours, an additional 20 cc. of a 1:1 mixture of acetic and concentrated hydrochloric acids being added in portions over that time. The toluene layer was separated, the toluene was evaporated, and the residue was sublimed at 200° and 0.4 mm. The sublimate crystallized from alcohol-acetone as colorless leaflets; yield, 0.81 g. (86%); m.p. 120-121°. After two further crystallizations from alcohol-acetone the compound melted at 120.5-121°.

Anal. Calc'd for $C_{19}H_{18}$: C, 92.7; H, 7.3.

Found: C, 92.3; H, 7.4.

The *picrate* crystallizes from absolute alcohol in yellowish-orange needles; m.p. 124-124.5°.

Anal. Calc'd for $C_{19}H_{18} \cdot C_6H_3N_3O_7$: N, 8.8. Found: N, 8.7.

1,4-Dimethylchrysene. To a Grignard reagent made from 0.5 cc. of methyl iodide and 0.15 g. of magnesium in 5 cc. of dry ether was added 0.5 g. of 1-methyl-4-keto-1,2,3,4-tetrahydrochrysene and 10 cc. of dry benzene. The mixture was allowed to stand at room temperature overnight and was then decomposed with ice and ammonium chloride. To the residue from evaporation of the benzene-ether layer was added 0.05 g. of palladium-charcoal catalyst (12) and the mixture was heated at 300-320° for one hour. The mixture was then taken up in benzene, the filtered benzene solution was evaporated, and the hydrocarbon was crystallized from benzene-petroleum ether; yield, 0.39 g. (79%); m.p. 140-141°. After two recrystallizations from benzene-petroleum ether, the compound was obtained as clusters of small, colorless needles; m.p. 141.5-142.5°.

Anal. Calc'd for $C_{20}H_{18}$: C, 93.8; H, 6.3.

Found: C, 93.6; H, 6.2.

The *picrate* crystallizes from absolute alcohol containing an excess of picric acid as deep red needles; m.p. 140.5-141°.

Anal. Calc'd for $C_{20}H_{18} \cdot C_6H_3N_3O_7$: N, 8.7. Found: N, 8.6.

γ -(1-Phenanthryl)butyric acid (VII). (a) To a suspension of 2.92 g. of β -(1-phenanthryl)propionic acid (VIII) (13) in 5 cc. of dry ether and 1 drop of pyridine was added 3.3 cc. of thionyl chloride. The mixture was allowed to stand at room temperature for a half hour and then the ether and thionyl chloride were evaporated under reduced pressure. The acid chloride was dissolved in a mixture of benzene and ether and added drop by drop to a solution of diazomethane in 60 cc. of dry ether, the

diazomethane being made from 7 cc. of ethyl N-methyl-N-nitrosocarbamate. After standing for two hours at room temperature, the ether and benzene were evaporated under reduced pressure and the crystalline diazo ketone was dissolved in 50 cc. of dry methanol. The methanol solution was refluxed for two hours (one hour was insufficient), with addition of silver oxide from 6 cc. of 10% silver nitrate solution over this time, a quarter at the beginning, another quarter in five portions at five minute intervals after this, another quarter at the end of the first hour, and the last quarter in five portions at five minute intervals after this. The methanol solution was filtered to remove the silver oxide, and the residue obtained from evaporation of the methanol was heated for an hour with an excess of 45% potassium hydroxide solution. The mixture was diluted to dissolve the potassium salts and then acidified. The precipitated acid was sublimed at 230° and 0.4 mm. and the sublimate was crystallized twice from dilute acetic acid; yield, 1.88 g. (61%); m.p. 153–154°. After several further crystallizations from dilute acetic acid, the acid separated as colorless leaflets; m.p. 154.5–155.5°.

(b) Five and seven-tenths grams of γ -[1-(1,2,3,4-tetrahydrophenanthryl)]butyric acid (IX) prepared from 1-keto-1,2,3,4-tetrahydrophenanthrene according to the procedure of Hoch (6) was esterified with an ethereal solution of diazomethane, the ether was evaporated, and the ester was heated for three hours at 250–260° with 0.55 g. of palladium-charcoal catalyst. The mixture was taken up in benzene, and the filtered benzene solution was evaporated. The ester was heated for one hour with 45% potassium hydroxide solution and the solution was diluted and acidified; weight, 5.42 g. (95%); m.p. 149–154°. After two crystallizations from dilute acetic acid, the compound melted at 154–155.5°. Hoch reports 152° as the melting point of this compound.

Anal. Calc'd for $C_{18}H_{16}O_2$: C, 81.9; H, 6.1.

Found: C, 81.5; H, 6.0.

1-Keto-1,2,3,4-tetrahydrochrysene (VI). To a suspension of 5.63 g. of the above acid in 60 cc. of dry ether and 2 drops of pyridine was added 12 cc. of thionyl chloride. After standing at room temperature for a half hour, the ether and thionyl chloride were removed under reduced pressure, the acid chloride was dissolved in 80 cc. of dry benzene, and 9 cc. of stannic chloride was added to the chilled solution. After standing for twenty minutes at room temperature, the mixture was hydrolyzed with ice and hydrochloric acid, the benzene layer was washed with ammonium hydroxide and then with water, the benzene was evaporated, and the ketone was crystallized from benzene; weight, 4.85 g. (92%); m.p. 226.5–228°. After two recrystallizations from benzene the compound was obtained as colorless prisms; m.p. 228–229°. Hoch gives 222° as the melting point of this compound:

Anal. Calc'd for $C_{18}H_{14}O$: C, 88.0; H, 5.7.

Found: C, 87.7; H, 5.7.

1-Methylchrysene (V). (a) A mixture of 0.69 g. of 1-methyl-1,2,3,4-tetrahydrochrysene and 0.07 g. of palladium-charcoal catalyst was heated at 300–320° for one hour and the mixture was taken up in benzene and filtered. The hydrocarbon obtained by evaporation of the benzene solution was crystallized from toluene; yield, 0.63 g. (94%); m.p. 248–250°. After two further crystallizations from toluene, colorless, glistening leaflets were obtained; m.p. 249.5–250°. The mixture melting point with chrysene (m.p. 246–247°) was 243–245°.

(b) To a Grignard solution made from 0.5 cc. of methyl iodide, 0.15 g. of magnesium, and 10 cc. of ether were added 0.5 g. of 1-keto-1,2,3,4-tetrahydrochrysene and 15 cc. of dry benzene. The mixture was allowed to stand at room temperature overnight and was then hydrolyzed with ice and ammonium chloride. The benzene-

ether layer was separated, the benzene and ether were evaporated, and the residue was heated for one hour with 0.05 g. of palladium-charcoal catalyst. The reaction-product was taken up in benzene, and the hydrocarbon obtained by evaporation of the filtered benzene solution was crystallized from benzene, giving colorless, glistening leaflets; weight, 0.42 g. (86%); m.p. 249.5–250°. The melting point was unchanged after two further crystallizations from benzene. The mixture melting point with the material prepared in part (a) was 249.5–250°. The mixture melting point with chrysene was 242.5–244°. The hydrocarbon, like chrysene, does not form a very stable picrate and we were unable to prepare a satisfactory picrate.

Anal. Calc'd for $C_{19}H_{14}$: C, 94.2; H, 5.8.

Found: C, 94.3; H, 5.8.

1-Ethylchrysene. To a Grignard solution made from 0.55 cc. of ethyl bromide and 0.15 g. of magnesium in 10 cc. of ether were added 0.5 g. of 1-ketotetrahydrochrysene and 15 cc. of dry benzene. The mixture was allowed to stand at room temperature for twelve hours, and ice and ammonium chloride were added to decompose the complex. The benzene-ether layer was evaporated and the residue was heated for one hour at 300–320° with 0.05 g. of palladium-charcoal catalyst. The mixture was taken up in benzene, the filtered solution was evaporated, and the hydrocarbon was crystallized from benzene-methanol; yield, 0.38 g. (73%); m.p. 183–184°. After two recrystallizations from benzene-methanol, colorless leaflets were obtained; m.p. 183.5–184°.

Anal. Calc'd for $C_{20}H_{16}$: C, 93.8; H, 6.3.

Found: C, 93.5; H, 6.1.

Methyl 1-keto-1,2,3,4-tetrahydrochrysene-2-glyoxalate (X). Sixty-nine hundredths gram of sodium was dissolved in 15 cc. of methanol and the excess methanol was then evaporated under reduced pressure. A mixture of 3 g. of 1-keto-1,2,3,4-tetrahydrochrysene and 3.6 g. of methyl oxalate was then added, the flask was filled with nitrogen, and 75 cc. of dry benzene was added. After the mixture had stood for five hours with occasional agitation, water and a few drops of 45% potassium hydroxide solution were added, the benzene layer was extracted twice with 2% potassium hydroxide solution, and the alkaline washings were acidified; weight, 3.92 g. (97%); m.p. 167–168°. After two crystallizations from benzene-methanol, deep yellow prisms were obtained; m.p. 176–177° with decomposition. Upon crystallization, two forms usually separate: light yellow, flocculent leaflets and thick, deep yellow prisms. On standing, the leaflets, which melt about 169–170°, change over almost completely to the prisms, and the remaining leaflets can be removed by decantation before filtering. The compound gives an immediate, reddish-brown color with alcoholic ferric chloride.

Anal. Calc'd for $C_{21}H_{16}O_4$: C, 75.9; H, 4.8.

Found: C, 76.0; H, 4.8.

1-Keto-2-carbomethoxy-1,2,3,4-tetrahydrochrysene (XI). A mixture of 2.90 g. of the above compound and 1.5 g. of powdered glass was heated at 180–190° for a half hour. The mixture was taken up in benzene and the filtered benzene solution was evaporated. The residue crystallized from benzene-methanol as colorless needles; weight, 2.10 g. (79%); m.p. 156–157.5°. After two recrystallizations from benzene-methanol the compound melted at 156.5–157.5°. This carbomethoxy ketone gives a green color on standing with alcoholic ferric chloride.

Anal. Calc'd for $C_{20}H_{16}O_3$: C, 79.0; H, 5.3.

Found: C, 79.2; H, 5.3.

1-Keto-2-methyl-2-carbomethoxy-1,2,3,4-tetrahydrochrysene (XII). To a solution of 0.3 g. of sodium in 10 cc. of methanol was added 1 g. of 1-keto-2-carbomethoxy-

1,2,3,4-tetrahydrochrysene in 30 cc. of benzene. The mixture was refluxed for two hours and then cooled. One and one-half cubic centimeters of methyl iodide was added and the mixture was allowed to stand at room temperature for an hour. Another 1.5 cc. of methyl iodide was then added and the mixture was refluxed for an hour, cooled, and acidified with acetic acid. The benzene and methanol were evaporated, benzene and water were added, the benzene layer was evaporated, and the residue was crystallized from benzene-methanol, giving colorless needles; weight, 0.93 g. (89%); m.p. 154–155°, unchanged after two further crystallizations. The melting point when the compound was mixed with the original 1-keto-2-carbomethoxytetrahydrochrysene was 125–135°. The compound gives no color with alcoholic ferric chloride.

Anal. Calc'd for $C_{21}H_{18}O_3$: C, 79.2; H, 5.7.

Found: C, 79.4; H, 5.7.

1-Keto-2-methyl-1,2,3,4-tetrahydrochrysene (XIII). A mixture of 0.75 g. of 1-keto-2-methyl-2-carbomethoxytetrahydrochrysene, 23 cc. of acetic acid, and 12 cc. of concentrated hydrochloric acid was refluxed for three hours, and then water was added to complete the precipitation of the ketone; weight, 0.59 g. (93%); m.p. 183–184.5°. After two crystallizations from benzene-methanol, colorless leaflets were obtained; m.p. 184–184.5°.

Anal. Calc'd for $C_{19}H_{16}O$: C, 87.7; H, 6.2.

Found: C, 87.5; H, 6.2.

2-Methyl-1,2,3,4-tetrahydrochrysene (XIV). A mixture of 0.2 g. of 1-keto-2-methyl-1,2,3,4-tetrahydrochrysene, 5 g. of amalgamated zinc, 10 cc. of acetic acid, 6 cc. of concentrated hydrochloric acid, and 2 cc. of toluene was refluxed for twenty-four hours. An additional 10 cc. of a 1:1 mixture of acetic and hydrochloric acids was added in portions over this period. The organic layer was evaporated, the residue was sublimed at 200° and 0.4 mm., and the sublimate was crystallized from alcohol-acetone, giving colorless, glistening leaflets; weight, 0.145 g. (77%); m.p. 145–146°, unchanged after two more recrystallizations. The mixture melting point with 2-methyl-1,2,3,4-tetrahydrochrysene (m.p. 141.5–142°) prepared from 2-methyl-4-keto-1,2,3,4-tetrahydrochrysene (1) was 143.5–145°.

β -(2-Phenanthroyl)- α -methylpropionic acid (XIX). A mixture of 0.5 g. of powdered sodium, 5.1 cc. of malonic ester, and 30 cc. of benzene was refluxed until the sodium had reacted. The suspension was cooled, 5 g. of ω -bromo-2-acetylphenanthrene (14) (XVIII) was added, and the mixture was allowed to stand at room temperature for twelve hours and then heated for three hours. Dilute hydrochloric acid was added to the cooled solution, the organic layer was evaporated, and the residue was heated for an hour with 45% potassium hydroxide solution. The mixture was diluted to dissolve the potassium salts and then acidified. The dicarboxylic acid was heated for an hour at 180–200° and the product was crystallized from acetic acid-toluene; yield, 1.8 g. (37%); m.p. 222–224°. After two further crystallizations from acetic acid-toluene, colorless needles with the melting point 228–229° were obtained.

Anal. Calc'd for $C_{19}H_{16}O_3$: C, 78.1; H, 5.5.

Found: C, 77.9; H, 5.5.

γ -(2-Phenanthroyl)- α -methylbutyric acid (XX). A mixture of 1 g. of β -(2-phenanthroyl)- α -methylpropionic acid, 5 g. of amalgamated zinc, 7.5 cc. of acetic acid, 7.5 cc. of concentrated hydrochloric acid, and 4 cc. of toluene was refluxed for twenty-four hours. An additional 7.5 cc. of concentrated hydrochloric acid was added in portions over this period. The organic layer was evaporated and the reduced acid was crystallized from benzene-petroleum ether; weight, 0.89 g. (94%); m.p. 122–124°.

After two recrystallizations from benzene-petroleum ether, colorless leaflets were obtained; m.p. 124–124.5°.

Anal. Calc'd for $C_{19}H_{18}O_2$: C, 82.0; H, 6.5.

Found: C, 82.1; H, 6.4.

Methyl 4-keto-1,2,3,4-tetrahydrochrysene-3-glyoxalate. Twenty-three hundredths gram of sodium was dissolved in 5 cc. of methanol and the excess methanol was removed under reduced pressure. A mixture of 1 g. of 4-keto-1,2,3,4-tetrahydrochrysene (XV) (1) and 1.2 g. of methyl oxalate was added, the apparatus was filled with nitrogen, and 25 cc. of dry benzene was added. After the mixture had stood at room temperature for three hours with occasional shaking, water and a few drops of 45% potassium hydroxide solution were added, the benzene layer was washed with 2% potassium hydroxide solution, and the alkaline washings were acidified; weight, 1.27 g. (95%); m.p. 112–115°. After three recrystallizations from acetone-methanol, lemon-yellow needles of melting point 116–117.5° were obtained. The compound gives an immediate, deep brown color with alcoholic ferric chloride.

Anal. Calc'd for $C_{21}H_{16}O_4$: C, 75.9; H, 4.8.

Found: C, 75.5; H, 4.7.

3-Carbomethoxy-4-keto-1,2,3,4-tetrahydrochrysene. A mixture of 0.59 g. of the above glyoxalate and 0.3 g. of powdered soft glass was heated for one hour at 180° and the decarbonylated product was taken up in benzene, the benzene solution was filtered, the benzene was evaporated, and the residue was crystallized from benzene-alcohol; weight, 0.44 g. (82%); m.p. 153–155°. After two further crystallizations from benzene-alcohol, colorless needles were obtained; m.p. 154–155°. This compound gives an emerald-green color on standing with alcoholic ferric chloride.

Anal. Calc'd for $C_{20}H_{16}O_3$: C, 79.0; H, 5.3.

Found: C, 78.8; H, 5.3.

3-Methyl-3-carbomethoxy-4-keto-1,2,3,4-tetrahydrochrysene. To a solution of 0.45 g. of sodium in 15 cc. of methanol was added 1.5 g. of 3-carbomethoxy-4-keto-1,2,3,4-tetrahydrochrysene in 30 cc. of benzene and the mixture was refluxed for two hours. To the cooled mixture was added 2.3 cc. of methyl iodide, and the reaction-mixture was allowed to stand at room temperature for an hour. Another 2.3 cc. of methyl iodide was then added and the whole was refluxed for an hour. The mixture was acidified with acetic acid and the benzene and methanol were evaporated. Water and benzene were added, the benzene layer was evaporated, and the residue was crystallized from acetone-methanol, giving colorless needles; weight, 1.32 g. (84%); m.p. 114–116°. After several recrystallizations from acetone-methanol, the melting point was 115.5–117°. The methylcarbomethoxy ketone gives no color with alcoholic ferric chloride.

Anal. Calc'd for $C_{21}H_{18}O_3$: C, 79.2; H, 5.7.

Found: C, 79.2; H, 5.7.

3-Methyl-4-keto-1,2,3,4-tetrahydrochrysene (XVI). (a) To a suspension of 0.75 g. of γ -(2-phenanthryl)- α -methylbutyric acid in 7.5 cc. of dry ether and 1 drop of pyridine was added 1.5 cc. of thionyl chloride and the mixture was allowed to stand at room temperature for a half hour. The ether and thionyl chloride were evaporated under reduced pressure, the acid chloride was dissolved in 7.5 cc. of carbon disulfide, and 1.2 cc. of stannic chloride was added to the solution cooled in ice-water. After standing at room temperature for ten minutes, the mixture was hydrolyzed with ice and hydrochloric acid and the carbon disulfide layer was evaporated. The residue was dissolved in benzene, the benzene solution was washed with ammonium hydroxide, the benzene was evaporated, and the ketone was crystallized from alcohol-acetone; m.p. 108–111°; weight, 0.45 g. (64%). After several recrystalliza-

tions from alcohol-acetone, the ketone was obtained as colorless prisms; m.p. 114–115°.

(b) A mixture of 2.1 g. of 3-methyl-3-carbomethoxy-4-keto-1,2,3,4-tetrahydrochrysene, 60 cc. of acetic acid, and 30 cc. of concentrated hydrochloric acid was refluxed for four hours. Water was added to the cooled mixture, which was then extracted with benzene. The benzene was evaporated, the residue was sublimed at 200° and 0.4 mm., and the sublimate was crystallized from alcohol-acetone; weight, 1.58 g. (92%); m.p. 114–115.5°. The mixture melting point with the material prepared in part (a) was 114–115.5°.

Anal. Calc'd for $C_{19}H_{16}O$: C, 87.7; H, 6.2.

Found: C, 87.2; H, 6.1.

3-Methyl-1,2,3,4-tetrahydrochrysene. A mixture of 1 g. of 3-methyl-4-keto-1,2,3,4-tetrahydrochrysene, 10 g. of amalgamated zinc, 20 cc. of acetic acid, 12 cc. of concentrated hydrochloric acid, and 5 cc. of toluene was refluxed for twenty-four hours, an additional 20 cc. of a 1:1 mixture of acetic and hydrochloric acids being added in portions over this period. The organic layer was evaporated, the residue was sublimed at 200° and 0.4 mm., and the sublimate was crystallized from benzene-petroleum ether, giving colorless needles; weight, 0.82 g. (86%); m.p. 129–130.5°. After several recrystallizations from benzene-petroleum ether, the hydrocarbon melted at 130–131°.

Anal. Calc'd for $C_{19}H_{18}$: C, 92.7; H, 7.3.

Found: C, 92.4; H, 7.3.

3-Methylchrysene (XVII). A mixture of 0.74 g. of 3-methyl-1,2,3,4-tetrahydrochrysene and 0.07 g. of palladium-charcoal catalyst was heated for one hour at 300–320°. The mixture was taken up in benzene, the filtered benzene solution was evaporated, and the residue was crystallized from benzene-petroleum ether, giving colorless, glistening leaflets; weight, 0.67 g. (92%); m.p. 170–170.5°, unchanged after several further crystallizations.

Anal. Calc'd for $C_{19}H_{14}$: C, 94.2; H, 5.8.

Found: C, 93.8; H, 5.8.

The *picrate* crystallizes from absolute alcohol as orange needles; m.p. 164–164.5°.

Anal. Calc'd for $C_{19}H_{14} \cdot C_6H_3N_3O_7$: N, 8.9. Found: N, 8.9.

β -[γ -(1,2,3,4-Tetrahydrophenanthroyl)]*propionic acid* (XXI). The combined mother liquors from the crystallizations of about 35 g. of crude β -[γ -(1,2,3,4-tetrahydrophenanthroyl)]*propionic acid* (8) deposited about 2 g. of crystals after standing for about two months at room temperature; m.p. 150–154°. After several recrystallizations from toluene-acetic acid, colorless, rhombic prisms of melting point 158–159° were obtained. Concentration of the filtered mother liquors did not give any more acid of this melting point and, although crops were obtained which melted over wide ranges, from 125–165°, no other pure products were isolated.

Anal. Calc'd for $C_{18}H_{18}O_2$: C, 76.6; H, 6.4.

Found: C, 76.8; H, 6.3.

γ -[γ -(1,2,3,4-Tetrahydrophenanthryl)]*butyric acid*. A mixture of 1 g. of the above keto acid, 2.5 g. of amalgamated zinc, 4 cc. of acetic acid, 4 cc. of concentrated hydrochloric acid, and 2 cc. of toluene was refluxed for twenty-four hours. An additional 4 cc. of concentrated hydrochloric acid was added in portions over this time. The organic layer was evaporated, and the residue was crystallized from benzene; weight, 0.80 g. (84%); m.p. 92–95.5°. After several crystallizations, colorless prisms of melting point 95.5–97° were obtained.

Anal. Calc'd for $C_{18}H_{20}O_2$: C, 80.6; H, 7.5.

Found: C, 81.1; H, 7.3.

The structure of the acid was proved by catalytic dehydrogenation to γ -(2-phenanthryl)butyric acid. Two-tenths gram of γ -[7-(1,2,3,4-tetrahydrophenanthryl)]-butyric acid was esterified with an ethereal solution of diazomethane, the ether was evaporated, and the ester was heated at 250–270° for two hours with 0.03 g. of palladium-charcoal catalyst. The mixture was taken up in benzene and filtered, the benzene was evaporated, and the residue was heated for an hour with 3 cc. of 45% potassium hydroxide solution. The mixture was diluted to dissolve the potassium salt and then acidified; weight, 0.162 g. (82%); m.p. 130–131°. After two crystallizations from benzene the acid melted at 133.5–134.5°. The mixture melting point with authentic γ -(2-phenanthryl)butyric acid (1) (m.p. 134–135°) was 134–135°.

4-Keto-1,2,3,4,7,8,9,10-octahydrochrysene (XXII). To a suspension of 0.24 g. of γ -[7-(1,2,3,4-tetrahydrophenanthryl)]butyric acid in 5 cc. of ether and 1 drop of pyridine was added 1 cc. of thionyl chloride. After standing for a half hour at room temperature, the ether and thionyl chloride were removed under reduced pressure, the acid chloride was dissolved in 3 cc. of dry benzene, and to the chilled solution was added 0.4 cc. of stannic chloride. After standing for ten minutes in the cold, the mixture was hydrolyzed with ice and hydrochloric acid, the benzene layer was washed with ammonium hydroxide, the benzene was evaporated, and the residue was crystallized from methanol, giving colorless leaflets; m.p. 91–94°; weight, 0.15 g. (68%). After several recrystallizations from methanol, the ketone was obtained as leaflets which melted at 93.5–95°. Sometimes on crystallization needles are obtained which melt at 89.5–91° and which remelt at 93.5–95°.

Anal. Calc'd for $C_{18}H_{18}O$: C, 86.4; H, 7.2.

Found: C, 86.1; H, 7.55.

4-Methylchrysene (XXIII). To a Grignard reagent prepared from 0.12 g. of magnesium and 0.40 cc. of methyl iodide in 10 cc. of dry ether was added 0.475 g. of 4-ketoöctahydrochrysene in 5 cc. of benzene. After standing at room temperature for twelve hours, the mixture was hydrolyzed with ice and hydrochloric acid, the benzene-ether layer was evaporated, and the residue was heated at 300–320° for one hour with 0.1 g. of palladium-charcoal catalyst. The mixture was taken up in benzene and filtered, the benzene was evaporated, and the residue was crystallized from benzene-petroleum ether; weight, 0.28 g. (61%); m.p. 147–149°. After sublimation and several recrystallizations from benzene-petroleum ether, the hydrocarbon melted at 149–149.5°. The mixture melting point with authentic 4-methylchrysene (1) showed no depression.

SUMMARY

The 1- and 3- methylchrysenes have been prepared, both by two independent syntheses.

New methods of preparation of 2- and 4- methylchrysenes are given.

ANN ARBOR, MICH.

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